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Measurement of the (pressure, density, temperature) relation of a (methane + nitrogen) gaseous mixture using an accurate single-sinker densimeter

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ABSTRACT

A single-sinker magnetic suspension densimeter based on Archimedes' buoyancy principle is described. Density measurements on high-purity nitrogen demonstrate the performance of the densimeter. Comprehensive (p, ρ, T) measurements at low densities on a gaseous mixture with mole fraction of $(0.8977CH_4 + 0.1023N_2)$ were carried out on this densimeter at six temperatures from (170.586 to 270.054) K and at pressures ranging from (0.1333 to 1.5945) MPa. The overall uncertainty in density is estimated to be 0.1%. The uncertainty in temperature is estimated to be 5 mK and that in pressure is 250 Pa for (0 to 1.5) MPa and 390 Pa for (1.5 to 3) MPa, respectively. The experimental results of the (methane + nitrogen) mixture were compared with REFPROP 9.0, which used GERG-2008 and AGA8 equations of state to predict thermophysical properties of natural gas. The absolute relative deviations of density measurements are all within 0.1%. Meanwhile the experimental results were correlated using the virial equation of state (Virial EOS) with three different mixing rules. The calculated results using the virial EOS combined with VDW mixing rule show good agreement with the experimental data.

1. Introduction

Methane (CH_4) and nitrogen (N_2) are two main components of natural gas, coal-bed gas, and biogas. Moreover, they are key components of multicomponent mixture refrigerants used in low-temperature Joule–Thomson refrigerators [1]. Thus, accurate prediction of thermophysical properties is important in many industry fields such as petrochemical engineering processing and refrigeration industry. These thermophysical properties can be calculated by an equation of state (EOS) regressed through vast numbers of experimental values. Among these experimental data, (p, ρ, T) values are of great importance which impact the accuracy of the EOS. Therefore, design of accurate density measurement apparatus is significant for both academic research and industry applications.

Densimeters based on conventional techniques, such as bellows volumometry, piezometers, isochoric methods, and vibrating bodies, have one or more of the following disadvantages: applicable only in limited density ranges, mechanical complexity, need of calibration with reference fluids over the entire operational range, and limited accuracy apart from a few exceptions, *etc.* [2]. Hydrostatic balance densimeters with magnetic suspension couplings based on Archimedes' buoyancy principle have many advantages, such as high accuracy, practicable without calibration fluids, covering both gas and liquid phases range, and practicable in wide ranges of temperature and pressure [3]. The two-sinker and single-sinker densimeter based on the magnetic suspension coupling technique were described in detail by Kleinrahm *et al.* in 1986 [4] and by Wagner *et al.* in 1995 [5], respectively. Several new accurate densimeters have been developed and selected fluids have been measured accurately by their group since 1980s [6–10].

Considering that the single-sinker densimeter is simple in design and can extend pressure ranges of application while retaining a very high accuracy, it has been used in many research institutions. Comprehensive (p, ρ, T) measurements on two gas mixtures of $(0.9CH_4 + 0.1N_2)$ and $(0.8CH_4 + 0.2N_2)$ at temperatures from (240 to 400) K and at pressures up to 20 MPa have been carried out by Chamorro *et al.* and the conclusion points out that the GERG-2004 equation of state for natural gases is far superior to AGA8-DC92 and ECS-SI models [11]. Accurate density measurements for a 91% methane natural gas-like mixture have been performed by Prashant *et al.* over the temperature ranges from (270 to 340) K and pressure ranges from (3.450 to 34.543) MPa. The conclusion shows that the AGA8-DC92 may have problems in some regions of the phase space [12].

In this work, (p, ρ, T) measurements of a $(0.8977CH_4 + 0.1023N_2)$ gaseous mixture were performed using a compact single-sinker densimeter along six different isotherms at temperatures from

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(170.586 to 270.054) K and at pressures from (0.1333 to 1.5945) MPa. The experimental results were compared with the densities calculated with REFPROP 9.0 [13] and correlated with virial EOS. The accuracy of the densimeter has been verified by pure nitrogen gas in our previous work [14].

2. Experimental apparatus

2.1. Principle of the single-sinker densimeter

The single-sinker densimeter is based on Archimedes' principle. The density of the fluid can be determined by the following equation:

$$\rho_{\text{fluid}} = \frac{m_s - W}{V_s(T,p)}, \tag{1}$$

where W is the "apparent" mass of the sinker when immersing in the fluid; m_s is the 'true' mass of the sinker in vacuum and V_s (T, p) is volume of the sinker under the state point (T, p) conditions.

The single-sinker densimeter was described in detail by Wagner and Brachthäuser based on a magnetic suspension device [5]. The basic construction of the magnetic suspension balance (MSB), which includes the comparator balance, measuring cell, sinker, magnetic suspension coupling (MSC) and controlling system, is shown in figure 1. The MSC consists of an electromagnet, a permanent magnet and a position sensor. The apparent weight of the sinker is transmitted to the balance by this coupling with a non-contact force transmission method. The measuring cell covers a wide T and p range because there is not direct contact between the fluid and the balance. The permanent magnet is in the measuring cell while the electromagnet hanging under the balance is in the atmosphere.

The stable suspended state of the permanent magnet is achieved by adjusting the current of the electromagnet through the position sensor and the controlling system. In the zero point (ZP) position, the permanent magnet is suspended at a relatively long distance from the top of the measuring cell and the sinker is not picked up by the bearing cone. In this way, the weight of the permanent magnet and auxiliary is transmitted to the balance. While in the measuring point (MP) position, the permanent magnet is suspended at a relatively short distance from the top of the measuring cell and the sinker is picked up by the bearing cone. So, the weight of the sinker, permanent magnet and auxiliary is transmitted to the balance. The 'apparent' mass of the sinker immersed in the measuring fluid is determined by subtracting the two weighing explained above. Therefore the density can be calculated by equation (1).

2.2. Description of the whole experimental system

Figure 2 shows the schematic drawing of the whole apparatus. It mainly consists of the following parts: MSB, thermostat system, temperature and pressure measuring system, sample filling system, vacuum and auxiliary systems. Each of these important parts is described in detail as follows.

The MSB used in this work is manufactured by Rubotherm Präzisionsmesstechnik GmbH. The resolution of the comparator balance (Sartorius CC111) is 1 µg. In order to reduce errors due to changes in the slope of the characteristic line, the balance has two compensating weights. One is made of tantalum (m_1 = 17.496 g) and the other is made of titanium (m_2 = 4.737 g). As shown in figure 1, the two weights are loaded on the balance pan at ZP and MP states, respectively. Hence the overall load difference between the two states is decreased. The two weights have different mass, but nearly the same volume, thus the buoyancy influence exerted by the ambient

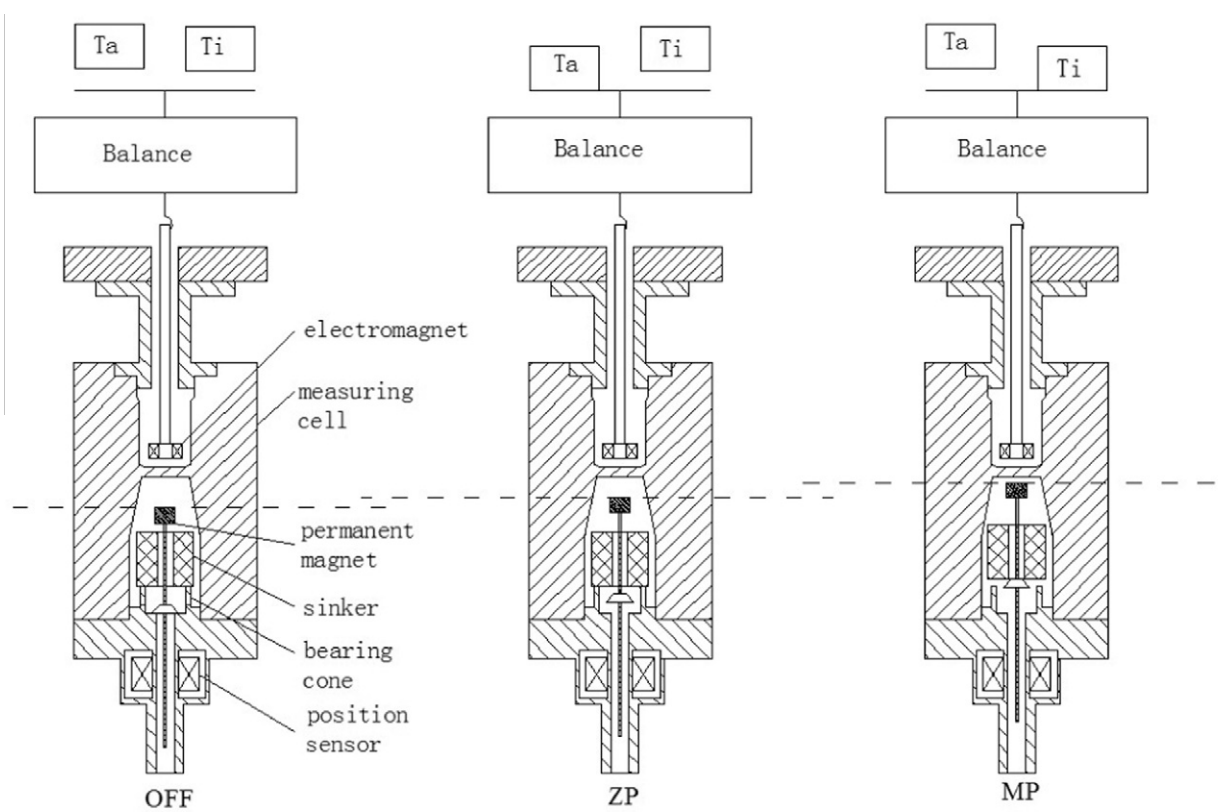

FIGURE 1. Basic design of the compact single-sinker densimeter.